Water: the most effective solvent for liquid-phase hydrodechlorination of chlorophenols over Raney Ni catalyst

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ABSTRACT

Catalytic hydrodechlorination (HDC) has proved to be an efficient approach to dispose chlorinated organic compounds (COCs). The influence of solvent on the HDC of chlorophenols with H_2 over Raney Ni catalyst was investigated. We found that protic solvents, especially water, significantly accelerated liquid-phase HDC that was sluggish in aprotic solvents. Among the selected solvents, water was the most effective solvent for liquid-phase HDC over Raney Ni catalyst. To study the mechanism for the rate acceleration in the HDC that was promoted by protic solvents, catalysts were characterized by SEM, EDX, and XRD techniques. It was found that solvent could affect surface composition and surface micro-topography of Raney Ni catalyst. On the basis of these studies, an effective and practical reaction system was developed to dispose chlorophenols over Raney Ni catalyst; a broad range of chlorophenols were efficiently hydrodechlorinated in aqueous solutions under mild conditions, and the catalyst could be reused at least five times without any loss of catalytic activity.

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1. Introduction

Chlorophenols are widely used in a number of important industrial processes such as production of germicides, algaecides, fungicides, herbicides, dyes, wood protectors, and plant growth regulators [1]. Because of the wide application of chlorophenols in numerous branches of chemical industry, chlorophenol contaminants have been found in soil, groundwater, and even in food chains [2,3]. Due to their high toxicity, low biodegradability, and persistence in the environment, chlorophenols are now established as a class of priority environmental pollutants by the US EPA [4]. Therefore, it is of crucial importance to develop an efficient method for transforming chlorophenols into non-hazardous products.

Over the last few years, various physical, biological, and chemical remediation methods have been developed for the degradation of chlorophenols [5–7]. Generally, biological treatment is superior to physical/chemical method that with high treatment costs and possibilities of secondary pollution [8]. However, biological treatment is prohibitively slow and affected by chlorophenols

toxicity, which strongly restricts its application field [9]. On the other hand, incineration is a well-established method for the elimination of chlorophenols, but it often leads to a large consumption of energy and formation of highly toxic by-products such as dioxins [9,10]. Advanced oxidation processes including Fenton, wet peroxide oxidation, supercritical water oxidation, nonthermal plasmas, and photochemical processes have been studied extensively in the last few years, showing good results but also have some drawbacks such as need of relatively high temperatures and/or pressures, large amount of reagents, and/or complex equipment [11–16]. Compared with the approaches mentioned above, catalytic hydrodechlorination (HDC) has economical and environmental advantages and is considered as a viable non-destructive method whereby the hazardous material is transformed into reusable hydrocarbons without toxic compounds formation [17–19].

The liquid-phase HDC of chlorophenols has been accomplished successfully using catalyst based on noble metals, such as Rh [19–21], Ru [22,23], Pt [24], and Pd [25–27]. Pd-based catalysts are regarded as the most active catalysts, but their high cost limited wide application [28]. In recent years, Raney Ni has received considerable attention in the HDC of organochlorines mainly because of its low cost and availability [29]. And, it has been proved that chlorinated organic compounds (COCs) could be completely

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hydrodechlorinated in liquid system over Raney Ni under mild conditions [29–31]. In liquid-phase HDC, methanol and ethanol have been the most frequently used solvent due to environmental applicability and/or reactant solubility considerations [28]. Moreover, it was reported that HDC rate could be improved greatly by adding water to solvents [32–35]. Given the abundance and low cost of water, as well as the fact that water is the solvent used by nature in biological chemistry, the use of water as a solvent is both economically and environmentally attractive [36–39]. Recently, water as a solvent has been used successfully in organic reactions, such as hydrogenation, oxidation, and cross-coupling reactions, and enables novel reactivity and/or speeds reactions [40–42]. So far, there are few studies that focused on liquid-phase HDC using water as the sole solvent over heterogeneous catalyst.

Our aim is to develop a practical and efficient reaction system for liquid-phase HDC of high-concentration chlorophenols over Raney Ni catalyst. In this paper, we compare the effect of different solvents on the HDC and study the influence of water addition on Raney Ni catalyst. We successfully applied water as solvent to liquid-phase HDC of a broad range of chlorophenol substrates. Moreover, the mechanism for solvent effects on Raney Ni catalyst was elucidated with the aid of characterization techniques including SEM, EDX, and XRD. In addition, the catalyst used in ethanol was treated by washing with water to expand the usage of water in liquid-phase reactions.

2. Experimental

2.1. Chemicals

Raney Ni (RTH-3110) catalyst used in this work was purchased from Dalian Tongyong Chemical Co., Ltd., Liaoning, China. The weight percentage of nickel and aluminum in the catalyst are more than 90% and less than 7%, respectively. The catalyst was not pretreated before all experiments and kept in water-sealing storage.

All chlorophenols (2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2,3-dichlorophenol, 2,4-dichlorophenol, 2,5-dichlorophenol, 2,6-dichlorophenol, 3,4-dichlorophenol, 3,5-dichlorophenol, and 2,4,6-trichlorophenol) used in experiments were purchased from Sigma-Aldrich with a minimum purity of 98%. The other reagents such as ethanol, methanol, i-propanol, n-hexane, toluene, and sodium hydroxide are of analytical grade and supplied by Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Deionized water was used in the reaction. The purity of hydrogen and nitrogen used in the experiments is more than 99.99%.

2.2. Catalytic procedure

All liquid-phase HDC were carried out in a three-neck flask as our previous report [35]. The reaction vessel (100 mL) was placed in a temperature-controlled heating water bath with a precision of ±0.5 °C. At the beginning of each experiment, 80 mL solution of 4-chlorophenol, stoichiometric NaOH, and Raney Ni were added into the flask. After the air in the flask was completely replaced by nitrogen, hydrogen was introduced by bubbling in solvent with a constant volumetric flow rate of 10 mL min^{-1}. Then the reaction mixture was stirred vigorously with a magnetic stirrer to start the reaction.

2.3. Analytical methods

The intermediate products in the HDC of chlorophenols were determined by GC/MS (Thermo Scientific ITQ 900) with a column of TR-5MS (30 m × 0.25 mm × 0.25 μm). The composition of the reaction/product mixture was analyzed by gas chromatography (Agilent 7890A), employing a flame ionization detector (FID) and a column of DB-1701 (30 m × 0.32 mm × 0.25 μm). Prior to analysis, the basic solution samples were neutralized with dilute CH$_3$COOH (ca. 0.2 mol L^{-1}). The operating parameters were as follows: FID temperature (280 °C), injection port temperature (280 °C), injection mode (split), injection volume (1 μL), carrier gas N$_2$ (>99.999%), constant flow rate (25 mL min^{-1}), and carrier gas pressure at column head (12 psi). Temperature program was 50 °C for 2 min, 10 °C min^{-1} to 180 °C, and then 25 °C min^{-1} to 250 °C followed by a 2 min hold. The detection limit was 1 pg mL^{-1}. Taking 4-chlorophenol as a representative reactant, the conversion is defined as

$$\text{Conversion}(\%) = \frac{C_{\text{4-chlorophenol},0} - C_{\text{4-chlorophenol}}}{C_{\text{4-chlorophenol},0}} \times 100 \tag{1}$$

where $C_{\text{4-chlorophenol},0}$ and $C_{\text{4-chlorophenol}}$ represent the initial concentration of 4-chlorophenol and the value at time t, respectively. And HDC rate is given as [43,44]:

$$\text{HDC rate} = \frac{n_{\text{4-chlorophenol}} \times \text{Conversion}}{n_{\text{Raney Ni}} \times \text{Reaction time}} \tag{2}$$

where $n_{\text{4-chlorophenol}}$ and $n_{\text{Raney Ni}}$ represent the total amount of substance of 4-chlorophenol and Raney Ni, respectively. The HDC rate is the average one within reaction time.

2.4. Characterizations

The catalysts after the reaction in the liquid-phase system were separated from the solution, washed with 95% ethanol, i-propanol, and n-hexane to remove adsorbed organic compounds, and dried in a N$_2$ flow at 200 °C prior to characterization analysis [35]. The surface morphology of fresh and used catalysts were characterized using a Hitachi S-4800 field emission scanning electron microscope (FE-SEM) coupled with an energy-dispersive X-ray spectrometer (EDXS, HORIBA EMAX Energy EX-350) used for chemical elemental analysis. X-ray diffractogram (XRD) patterns of the catalysts were recorded on a Shimadzu XRD-6100 using a Cu Kα radiation operating at 40 kV and 30 mA. The samples were scanned at a rate of 0.1°/s over the 5° ≤ 2θ ≤ 80° range with a scan time of 5 s step^{-1}.

3. Results and discussion

3.1. Solvent effects in the HDC of 4-chlorophenol over Raney Ni catalyst

We began by examining Raney Ni-catalyzed liquid-phase HDC of 4-chlorophenol in an assortment of solvents, including methanol, ethanol, i-propanol, n-hexane, and toluene (Fig. 1). It can be seen that 4-chlorophenol could be hydrodechlorinated in these solvents, and the conversion exhibits a strong dependence on solvent with the following order: methanol > ethanol > i-propanol > n-hexane > toluene. Moreover, Raney Ni catalysts possess higher activities in alcohols than that in n-hexane and toluene, which implies that protic solvents are much better solvents for liquid-phase HDC compared with aprotic solvents. Our experimental data were consistent with the results reported by Xia et al. for the HDC over Pd/C catalyst [32]. Many researchers ascribed this to the fact that alcohols could play a role as hydrogen donor in liquid-phase HDC [45,46]. In the case of alcohols as solvent, the sequence of HDC rate was consistent with the order of dielectric constant (ε), dipole moment (μ), and normalized empirical parameter for solvent polarity (E_T^N) (Table 1) [47,48]. This suggested that HDC rate increased with solvent polarity for the HDC carried out in protic solvents.

Water possesses a higher ε and a greater μ than alcohols (Table 1), and it is a protic solvent with the strongest polarity
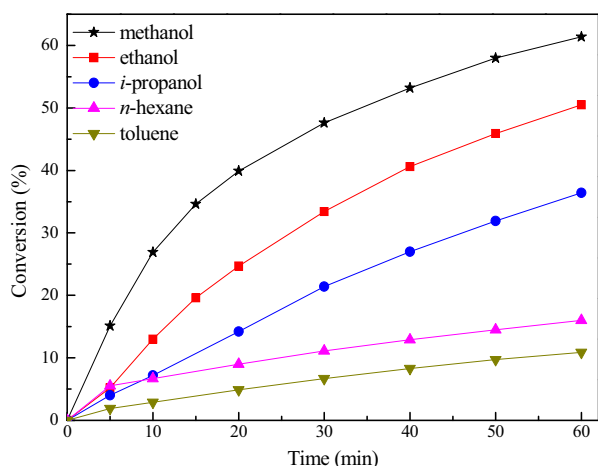
Fig. 1. HDC of 4-chlorophenol in various solvents over Raney Ni catalyst with reaction time. Reaction conditions: solvent (80 mL), 4-chlorophenol (0.8 g, 6.22 mmol), NaOH (0.274 g, 6.85 mmol), Raney Ni (0.24 g), temperature (30 °C), H2: 10 mL min⁻¹.

Table 1
The polarity parameters of protic solvents [47,48].

Solvent	E_T^N	ε	μ
i-Propanol	0.546	20.18	1.66
Ethanol	0.654	25.3	1.69
Methanol	0.762	33.0	1.70
Water	1.000	80.10	1.85

(E_T^N = 1.000, the upper limit of the scale for the empirical polarity parameter). Solvent polarity could be altered through changing proportion of water in alcohols. In other words, water–alcohol mixed solvent with higher water content has higher polarity. Thus, the mixed solvents were chosen to study the effect of solvent polarity to liquid-phase HDC over Raney Ni catalyst. Here, a series of water–ethanol mixed solvents, including ethanol, 20% water–ethanol (20/80, v/v), 50% water–ethanol (50/50, v/v), 80% water–ethanol (80/20, v/v), and water were used in catalytic HDC of 4-chlorophenol over Raney Ni catalyst. Fig. 2a shows the time dependence of 4-chlorophenol conversion in various water–ethanol solvents. It is noteworthy that the highest HDC rate of 4-chlorophenol is achieved in water, followed by 80% water–ethanol (80/20, v/v), 50% water–ethanol (50/50, v/v), 20% water–ethanol (20/80, v/v), and ethanol. This indicated that HDC rate increased with polarity of ethanol–water mixed solvents. It
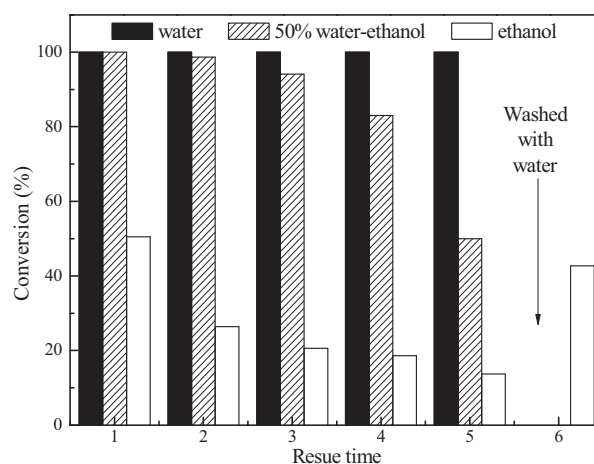

Fig. 3. Repeated HDC of 4-chlorophenol over Raney Ni catalyst in water, 50% water–ethanol (50/50, v/v), and ethanol for 60 min. Reaction conditions: solvent (80 mL), 4-chlorophenol (0.8 g, 6.22 mmol), NaOH (0.274 g, 6.85 mmol), Raney Ni (0.24 g), temperature (30 °C), H2: 10 mL min⁻¹.

is apparent that HDC rate could be changed remarkably by means of adding water to adjust the polarity of solvent. To further verify the influence of solvent polarity, HDC of 4-chlorophenol were carried out in water-*i*-propanol mixed solvents. As shown in Fig. 2b, similar results were observed in the HDC of 4-chlorophenol carried out in water–*i*-propanol mixed solvents. The results confirmed that HDC rate increased with the polarity of water–alcohol mixed solvent increasing. Moreover, the highest HDC rate of 4-chlorophenol was achieved in water, which is a protic solvent with the strongest polarity.

3.2. Water, the most effective solvent for the HDC of chlorophenols over Raney Ni catalyst

In order to evaluate stability of Raney Ni catalyst, catalytic HDC of 4-chlorophenol was repeated several times with the catalyst recovered after each reaction in water, 50% water–ethanol (50/50, v/v), and ethanol, respectively (Fig. 3). In ethanol, the conversion of 4-chlorophenol is 50.5% within 60 min using fresh catalyst and then gradually drops to 13.7% in the 5th run. In 50% water–ethanol (50/50, v/v), the conversion is 100% within 60 min for the first time, but drops to 50% in the 5th run. Yet in water, the conversion remains 100% even after five recycles, indicating good activity and
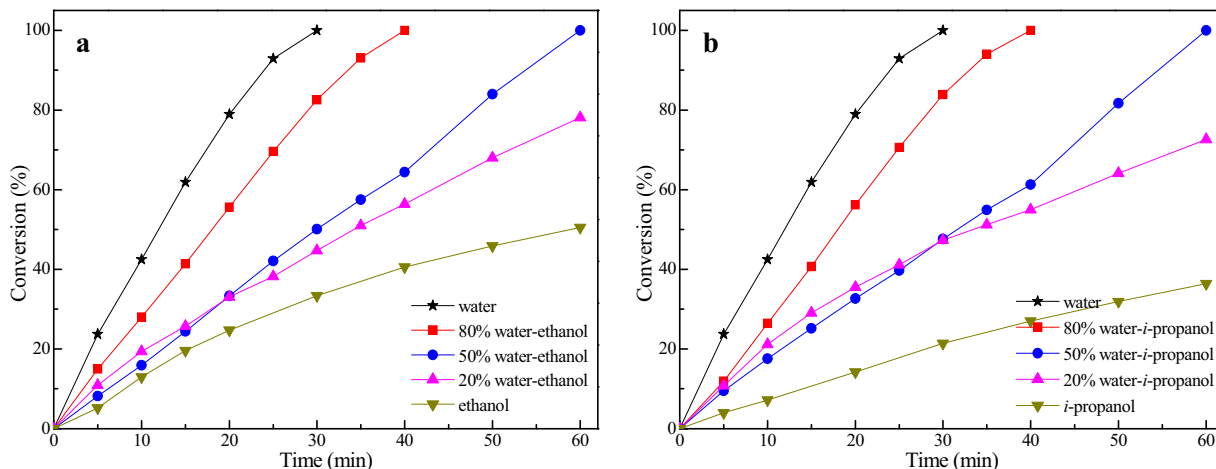

Fig. 2. HDC of 4-chlorophenol in water–ethanol (a) and water–*i*-propanol (b) mixed solvents. Reaction conditions: each solvent (80 mL), 4-chlorophenol (0.8 g, 6.2 mmol), NaOH (0.274 g, 6.85 mmol), Raney Ni (0.24 g), temperature (30 °C), H2: 10 mL min⁻¹.

Table 2
HDC of chlorophenols in aqueous solutions at room temperature.

Entry[a]	Chlorophenol	Temperature (°C)	Time (min)	HDC rate[b] (min^{-1})	Yield of product (%)[c]
1	2-Chlorophenol	30	35	0.044	Phenol (100)
2	3-Chlorophenol	30	30	0.051	Phenol (100)
3	4-Chlorophenol	30	30	0.051	Phenol (100)
4	2,3-Dichlorophenol	40	60	0.026	Phenol (100)
5	2,4-Dichlorophenol	40	60	0.026	Phenol (100)
6	2,5-Dichlorophenol	40	60	0.026	Phenol (100)
7	2,6-Dichlorophenol	40	60	0.025	Phenol (96.5), 2,6-DCP (3.5)
8	3,4-Dichlorophenol	40	60	0.026	Phenol (100)
9	2,4,6-Trichlorophenol	40	150	0.009	Phenol (92.8), 2,6-DCP (0.8), 2,4-DCP (6.4)

[a] Reaction conditions: solvent (80 mL), chlorophenols (6.22 mmol organic-Cl), NaOH (0.274 g, 6.85 mmol), Raney Ni (0.24 g), H$_2$: 10 mL min^{-1}.

[b] HDC rate = chloride atom removal rate = $\frac{n_{\text{organic-Cl}} \times \text{chloride atom removal ratio}}{n_{\text{Raney Ni}} \times \text{Reaction time}}$. The HDC rate was the average one within total reaction time here.

[c] Yields of products were determined by GC-MS.
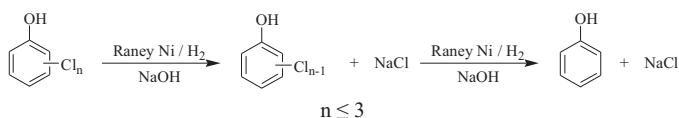
Scheme 1. The equation of the HDC of chlorophenols.

stability of the catalyst. These results suggested that Raney Ni catalyst exhibited higher activity and stability for liquid-phase HDC of 4-chlorophenol in water than that in alcohols and alcohol–water mixed solvents. In this context, it could be concluded that water was the best solvent among the solvents used in this work for the HDC of 4-chlorophenol over Raney Ni catalyst.

Furthermore, catalytic HDC of various chlorophenols at high concentration was carried out in aqueous solutions with Raney Ni catalyst to test the applicability of water as the sole solvent (Table 2). With the analysis of GC/MS, it was found that chlorophenol was efficiently hydrodechlorinated to produce phenol, and no cyclohexanone and cyclohexanol were detected. The reaction pathway involves multisteps that high chlorinated chlorophenols are dechlorinated to produce lower chlorinated chlorophenols, and then the lower chlorinated chlorophenols are further dechlorinated to form phenol (Scheme 1). For all the chlorophenols listed in Table 2, the HDC rates (chloride atom removal rates) follow the order of monochlorophenol > dichlorophenol > trichlorophenol. It is obvious that HDC rate of chlorophenols decreases with the increase in chlorine atom number. Overall, the chlorophenols listed in Table 2 could be effectively hydrodechlorinated over Raney Ni catalyst under normal pressure in water. These results confirmed that it was an effective method to dispose high-concentration chlorophenols with Raney Ni catalyst in water, and the catalyst could possess high activity and stability for the HDC of chlorophenols in water.

3.3. Characterization of Raney Ni catalyst used in different solvents

As mentioned above, Raney Ni catalyst exhibits higher activity and stability in water than that in organic solvent and water–alcohol mixtures. The results further indicate that solvent plays an important role on the reactivity of liquid-phase HDC. In liquid-phase reaction, solvent could influence reaction rate and product selectivity significantly in addition to acting as a reaction medium [32,48–50]. Indeed, the role of solvent known as solvent effects is one of the most central topics and has been widely studied [48]. Xia et al. [32] linked variations in HDC rate to solvent–reactant steric and π–resonance interactions that influenced reactant adsorption on the catalyst. Gómez-Quero et al. [51,52] attributed HDC activity dependency on ε to capacity of solvent to stabilize the arenium intermediate. In an attempt to clarify

the influence of solvent to Raney Ni catalyst, catalyst characterizations (SEM, EDX, and XRD) were introduced to analyze samples of Raney Ni catalysts before and after HDC.

Fig. 4 shows the representative SEM images of Raney Ni catalysts before and after HDC in water, 50% water–ethanol (50/50, v/v), and ethanol. As illustrated in Fig. 4a–e, the surfaces of Raney Ni catalysts reused in water and 50% water–ethanol (50/50, v/v) are almost the same as that of the fresh catalyst. Compared with the fresh catalyst (Fig. 4a), the surfaces become smooth with repeated use of the catalysts in ethanol (Fig. 4f and g). There should be some changes on the surfaces of Raney Ni catalysts used in ethanol. Subsequently, SEM-EDX analyses of Raney Ni catalysts were performed to obtain information about elemental composition of the catalyst surface (Fig. 5). For Raney Ni catalysts before and after the HDC, the characteristic peaks of Ni and Al are present in EDX spectra of all the catalysts, which revealed that elements of Ni and Al existed in all the catalysts. As shown in Fig. 5, there is no other peak in the samples of the catalysts used in water and 50% water–ethanol (50/50, v/v), indicating that the elemental composition of the catalyst surface did not change. And there are additional peaks for elements of Na and Cl in the samples of the catalysts used in ethanol. Hence, the elemental composition of catalyst surface was different for Raney Ni catalysts before and after HDC in ethanol.

To obtain further information about the catalyst surface composition, XRD analysis was performed for Raney Ni catalysts before and after HDC (Fig. 6). For the XRD patterns of Raney Ni catalysts before and after HDC, the peaks at $2\theta = 44.5°$, $51.8°$, and $76.3°$ could be indexed to (1 1 1), (2 0 0), and (2 2 0) planes of metallic nickel, respectively [53]. Except for peaks of Ni, no peak is found in the XRD pattern of Raney Ni catalysts used in water and 50% water–ethanol (50/50, v/v). Compared with the XRD pattern of fresh catalyst, there are five more peaks at $2\theta = 31.7°$, $45.5°$, $56.5°$, $66.4°$, and $75.4°$ in the XRD pattern of Raney Ni catalysts used in ethanol. According to JCPDS (Joint Committee on Powder Diffraction Standards) standard card, the five peaks are identified to (2 0 0), (2 2 0), (2 2 2), (4 0 0), and (4 2 0) NaCl planes, respectively. These results confirmed that some substrates coated surface of the catalysts used in ethanol and these substrates were NaCl crystals.

It is well established that HCl as a by-product, which is generated in liquid-phase HDC, is the main reason for catalyst deactivation [54]. For liquid-phase HDC, base is always used to serve as a proton scavenger, eliminating the negative effect of HCl on the catalyst [55,56]. In this work, NaOH was added to avoid catalyst deactivation caused by HCl, and NaCl was produced from neutralization of HCl and NaOH. According to the characterization analyses (SEM, EDX, and XRD), NaCl, produced in situ, would deposit on the surface of Raney Ni catalyst due to its poor solubility in ethanol [57]. With repeated use of the catalyst, more and more NaCl accumulates on surface of Raney Ni catalyst (Figs. 4–6). The accumulation of NaCl could block catalytic active sites and hinder the adsorption
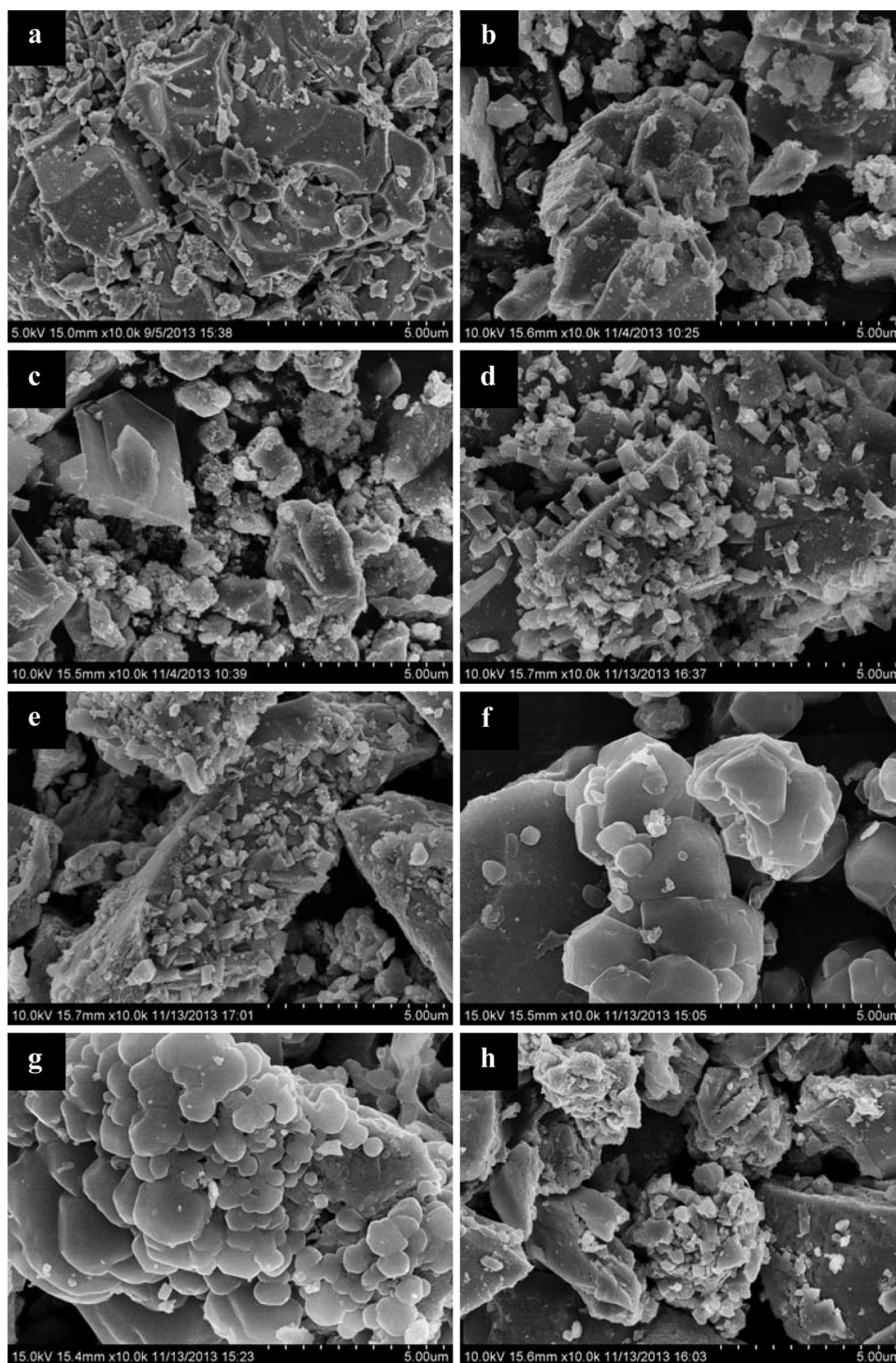
Fig. 4. SEM of (a) fresh Raney Ni catalyst, (b) Raney Ni catalyst used in water for once, (c) Raney Ni catalyst used in water for five times, (d) Raney Ni catalyst used in 50% water–ethanol (50/50, v/v) for once, (e) Raney Ni catalyst used in 50% water–ethanol (50/50, v/v) for five times, (f) Raney Ni catalyst used in ethanol for once, (g) Raney Ni catalyst used in ethanol for five times, and (h) Raney Ni catalyst (g) washed with water for 30 min.

and activation of hydrogen gas and chlorophenols, leading to the deactivation of Raney Ni catalyst. On the other hand, water as the reaction medium, having a better solubility to NaCl, could prevent NaCl from depositing on the surface of catalyst. Accordingly, Raney Ni catalyst keeps high activity and stability in water for liquid-phase HDC (Fig. 2). For protic solvents such as water, methanol, ethanol, and i-propanol, the solubility of NaCl in solvents increases with solvent polarity (Table 3) [58–60], and the activity of Raney Ni catalysts for the HDC carried out in protic solvents increases

Table 3
Solubility of NaCl in different solvents (25 °C) [58–60].

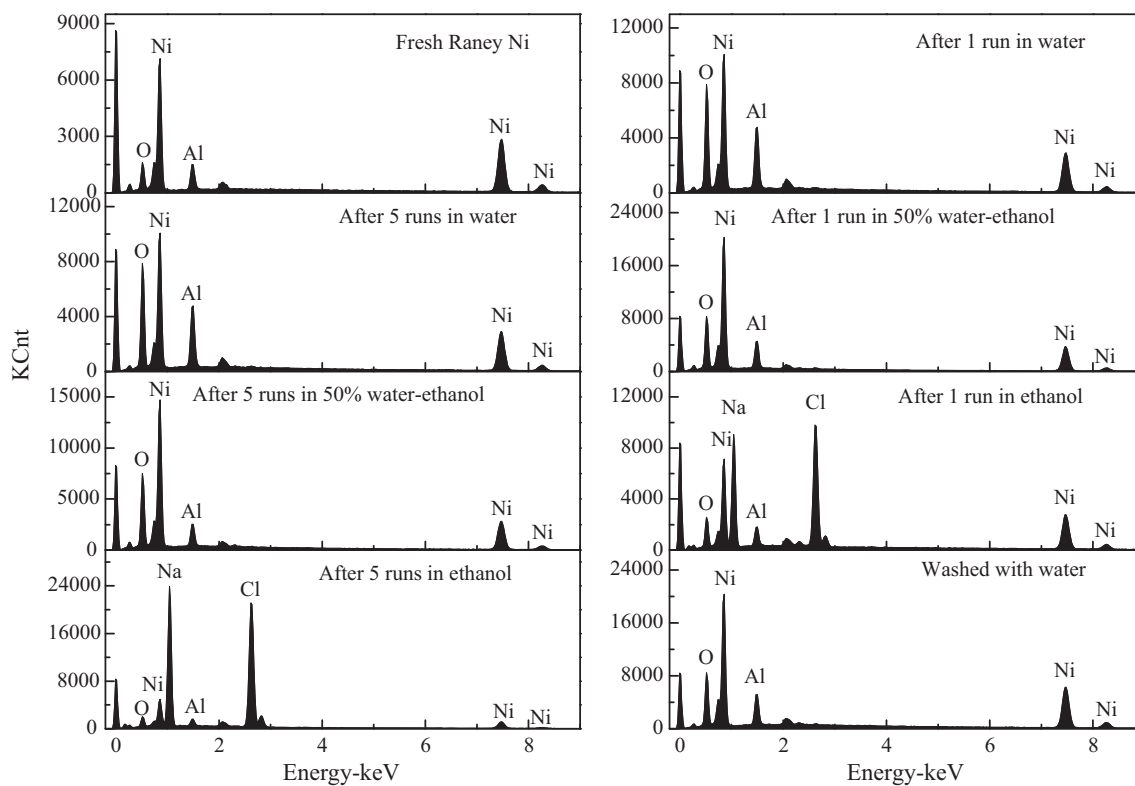| Solvent	Grams of salt per 100 g of solvent			
	i-Propanol	Ethanol	Methanol	Water
Solubility	0.0041	0.0658	1.375	26.483

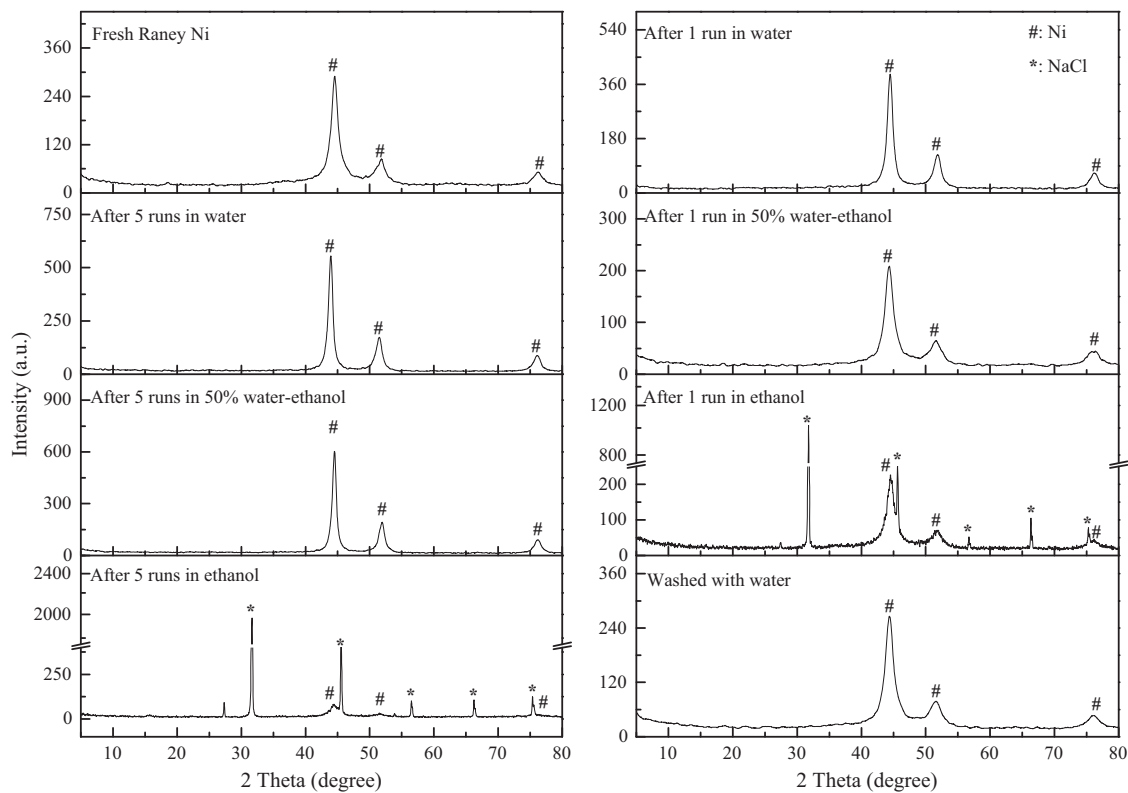**Fig. 5.** EDX images of fresh and used Raney Ni catalysts.

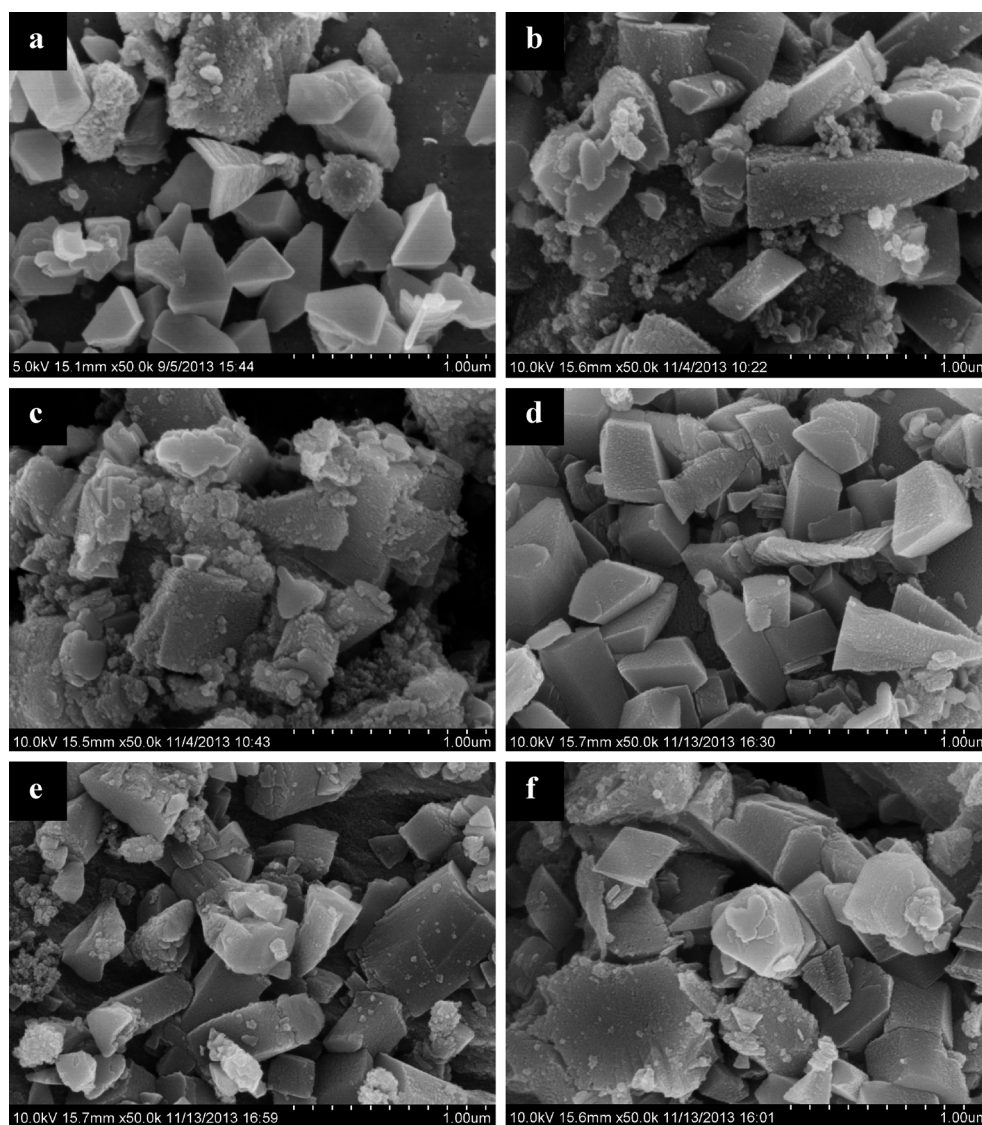**Fig. 6.** XRD patterns of fresh and used Raney Ni catalysts.

Fig. 7. SEM of (a) fresh Raney Ni catalyst, (b) Raney Ni catalyst used in water for once, (c) Raney Ni catalyst used in water for five times, (d) Raney Ni catalyst used in 50% water–ethanol (50/50, v/v) for once, (e) Raney Ni catalyst used in 50% water–ethanol (50/50, v/v) for five times, (f) after washed Raney Ni catalyst used in ethanol for five times with water for 30 min.

in order of *i*-propanol < ethanol < methanol < water. This should be an important reason why Raney Ni catalysts show various activities in different solvents. These results demonstrated that Raney Ni catalyst exhibited higher catalytic activity in the solvent, which could dissolve NaCl effectively in liquid-phase HDC. Moreover, NaCl accumulated on the surface of Raney Ni catalysts used in organic solvents and thus led to deactivation of the catalysts. We reported previously that, in the HDC over Pd/C catalyst carried out in organic solvents, the accumulation of NaCl could block catalytic active sites and thereby caused the decline in activity and stability of Pd/C catalyst [35]. Thus, the deactivation of the catalyst used in organic solvents, which was caused by the accumulation of inorganic salts, such as NaCl, was a universal phenomenon in liquid-phase HDC.

Whether the deactivation of Raney Ni catalyst used in ethanol could be recovered with water or not? In order to expand the usage of water in liquid-phase reaction, we treated the catalyst used in ethanol. The Raney Ni catalyst used in ethanol for five times was stirred in water (80 mL) at 30 °C for 30 min. Then, SEM, EDX, and XRD analyses were applied to observe the changes in surface and composition of the catalyst washed with water. As illustrated in Fig. 4h, the surface of Raney Ni catalyst washed with water is almost

the same as that of the fresh catalyst. According to EDX and XRD spectra (Figs. 5 and 6), NaCl, deposited on the surface of Raney Ni catalyst used in ethanol, can be removed by washing with water, in accordance with the SEM image (Fig. 4). Meanwhile, the conversion of 4-chlorophenol over Raney Ni used in ethanol after this treatment increases to 42.7%, which revealed that catalytic activity could be recovered partially by treating the catalyst with water.

Water as a solvent could prevent the deactivation of Raney Ni catalyst, which is caused by NaCl produced *in situ*. Moreover, 50% ethanol–water (50/50, v/v) could also prevent NaCl from depositing on the surface of catalyst, but the activity and stability of Raney Ni catalyst decreases as the repeated use of the catalyst. In order to find the reason for this phenomenon, Raney Ni catalysts before and after HDC were observed using SEM under high magnification (Fig. 7, see more details in the Supporting Information, Fig. S1). Compared with fresh catalyst, the surface micro-topography of Raney Ni catalysts used in water becomes much rougher with repeated use of the catalyst (Fig. 7). Yet, the surface micro-topography of Raney Ni catalysts used in 50% water–ethanol (50/50, v/v) does not changed obviously (Fig. 7d and e). Meanwhile, after Raney Ni catalyst used in ethanol being washed with water, the surface micro-topography

of the catalyst is almost the same as the fresh catalyst (Fig. 7f). The observations supported that the surface micro-topography of Raney Ni catalyst could be affected by solvent. In water, the surface micro-topography of Raney Ni catalyst became much rougher, which possibly led more and more active sites of the catalyst to be uncovered. This might be the reason why Raney Ni catalyst could keep higher activity and stability in water than that in 50% water–ethanol (50/50, v/v).

4. Conclusions

The results presented in this paper could be summarized as follows:

1. In liquid-phase HDC, protic solvents were better solvents compared with aprotic solvents, and HDC rate increased with solvent polarity increasing for the HDC carried out in protic solvents. Water, a protic solvent with the strongest polarity, was the most effective solvent for liquid-phase HDC of chlorophenols with Raney Ni catalyst. Moreover, Raney Ni catalyst exhibited much higher activity and stability in water than that in organic solvent and water–alcohol mixed solvents.
2. The results of catalyst characterizations (SEM, EDX, and XRD) demonstrated that inorganic salts, such as NaCl, produced in situ, could deposit on the surface of Raney Ni catalyst, and thus caused deactivation of the catalyst in organic solvents. Meanwhile, water as the reaction medium could prevent NaCl produced in situ from depositing on the surface of Raney Ni catalyst and enabled the catalyst to keep high activity and stability in the HDC.
3. According to the analysis of SEM under high magnification, it was found, for the first time, that the surface micro-topography of Raney Ni catalyst could be affected by solvent in liquid-phase HDC. This presumably accounted for the higher activity and stability of Raney Ni catalyst in water than that in water–alcohol mixed solvents.

In summary, water was the most effective solvent for disposing high-concentration chlorophenols over Raney Ni catalyst under mild conditions (30–40 °C, 1 atm). In water, a variety of chlorophenols could be efficiently hydrodechlorinated, and high catalytic activity and stability could be preserved.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2014.10.035.

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